

# Treatment of black liquor from the papermaking industry by acidification and reuse

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**Abstract:** Two different kinds of black liquor from the papermaking industry were treated by acidification and reuse. The experimental parameters and conditions were discussed in detail. The experimental results indicated that the treatment process mentioned in this article is an effective process for the treatment of black liquor from the papermaking industry. By the treatment, the solid materials in black liquor are transferred into two by-products and the other components are reused or evaporated. Thus, no wastewater except some condensation water would be discharged in pulping process and the problem of pollution of black liquor would be effectively solved.

**Keywords:** black liquor; acidification; reuse; lignin; water-reducing agent

## Introduction

Black liquor from pulping process in the papermaking industry is one of the most difficult industry wastewater to treat owing to its high color and very high chemical oxygen demand(COD<sub>Cr</sub>). On average, COD<sub>Cr</sub> value of black liquor (Be'6—7, 30℃) is about 100000 mg/L. Because lignin, one of the main pollutants and color materials of black liquor, is very difficult to biodegrade, biotreatment is improper to treat black liquor.

At abroad, alkali recovery has been extensively used to treat black liquor. From the 1960's, alkali recovery has been introduced to China and most of big papermaking factories have implemented projects of alkali recovery(Pan, 1996). However, the technology of alkali recovery is only suitable for big scale factories(Tang, 1996). In China, there are thousands of small or middle scale papermaking factories. Moreover, these factories mostly use straw as fiber material. On account of the high content of Si in straw and the small scale, many papermaking enterprises have not found a proper method to treat their wastewater in pulping process. With the more tension of environmental protection, those enterprises have confronted with the crisis of existence and improvement and they are looking for a appropriate treatment method, which ought to be not only suitable for their scales and straw material, but also feasible in economics.

In this paper, two kinds of black liquor with pine chips and bamboo chips as raw materials were treated by acidification and reuse. By the treatment, the solid materials in black liquor were transferred into two by-products(i.e. lignin and water-reducing agent), which have extensive uses and can bring economic benefits in good management and marketing(Mu, 2000).

## 1 Materials and method

### 1.1 Experimental materials

Two kinds of black liquor from varied raw materials i.e. pine chips and bamboo chips, were treated in the experiment. Those black liquors were taken from two papermaking factories which both use alkaline method in pulping and the major characteristics of theirs are shown in Table 1.

Table 1 Major characteristics of two kinds of black liquor

Raw materials	Be'	pH	Solid content, %	COD <sub>Cr</sub> , mg/L	SiO <sub>2</sub> , g/L	Lignin, g/L
Pine	5.7	13.4	8.2	92700	0.20	23.7
Bamboo	4.9	13.2	7.9	67000	0.59	19.6

### 1.2 Experimental procedure

The scheme of the experimental treatment process is given in Fig.1.

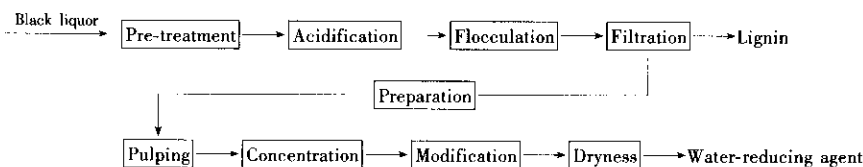


Fig.1 Scheme of the experimental treatment process

The experimental treatment process comprises three main units i. e. lignin extraction, recycling pulping and water-reducing agent preparation. Black liquor pre-treated by filtrating is acidified with  $\text{SO}_2$  to a certain pH. The mixture is then charged into a lignin reactor. In the reactor, the mixture is heated to a desired temperature and kept at this temperature for several hours. By this process, the exiguous lignin separated out in the acidification process would congregate into floc, so the mixture can be separated into solid and acid liquor by filtrating. The solid is then dried to a product called lignin. The liquor is prepared with some pulping reagents and reused in pulping process. The recycled liquor from recycling pulping is concentrated, modified and dried to another product called water-reducing agent.

## 2 Results and discussion

### 2.1 Effects of pH on lignin removals

Because lignin is the poorly biodegradable pollutant of black liquor and affects the process of recycling pulping, the lignin removals are used to test the efficiency of acidification. Fig.2 and Fig.3 respectively showed the lignin removals of pine and bamboo black liquor when they were acidified from pH 7.0 to pH 2.0. The initial pH of pine and bamboo black liquor was 13.4 and 13.2 respectively. The lignin removal is defined as the difference between the initial lignin content and its value at a given pH divided by its initial amount. The initial lignin content of pine black liquor was 23.7 g/L and that of bamboo black liquor 19.6 g/L. It can be seen that the lignin removals increased significantly when the black liquors were acidified to pH 3.5—4.0, below which there was very little change in lignin removals. This implies that the acidification has almost completed when the pH values reach 3.5—4.0. Furthermore, the trends of the two kinds of black liquor are quite parallel when they are treated by acidification with  $\text{SO}_2$ .

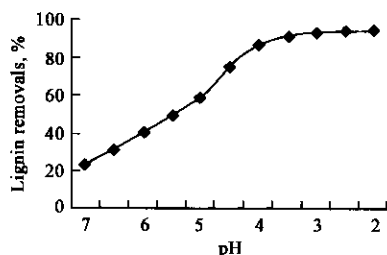


Fig.2 Effects of pH on lignin removals for pine black liquor

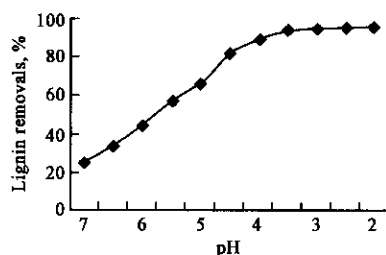


Fig.3 Effects of pH on lignin removals for bamboo black liquor

### 2.2 Effects of flocculation temperature on lignin removals

Since the results of flocculating reaction are different at diverse temperatures, the lignin removals were examined when the mixture were heated to a certain temperature and kept at this temperature for 3 h. The effect of flocculation temperature on the flocculation reaction is given in Fig.4. Fig.4 shows that heating could help lignin conglomerated, but the lignin removals decrease when the flocculation temperature is above  $70^\circ\text{C}$ . Therefore, the proper flocculation temperature would be selected at  $60\text{--}70^\circ\text{C}$ .

### 2.3 Effects of flocculation time on lignin removals

Having selected the flocculation temperature, the researchers examined the lignin removals when the flocculation time took from 1 to 5 h. Fig.5 gave the results. The lignin removals of pine black liquor varied from 63.2% to 93.8% and that of bamboo black liquor from 64.3% to 95.7%. Fig.5 also shows that there is very little change in the lignin removals when the time is over 3 h.

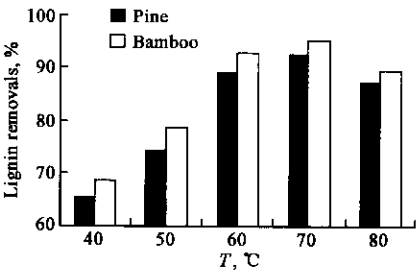


Fig. 4 Effects of flocculation temperature on lignin removals for black liquors

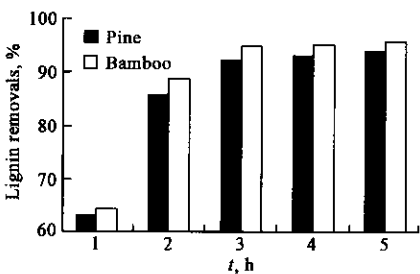
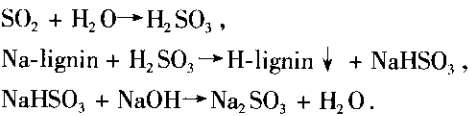


Fig. 5 Effects of flocculation time on lignin removals for black liquors at 70°C

2.4 Pulping conditions and results of reusing treated black liquor

When the liquor separated from filter is neutralized by NaOH, Na<sub>2</sub>SO<sub>3</sub> is formed through following chemical reactions:



Treated by acidification and preparation, the liquor is composed of 40—50 g/L Na<sub>2</sub>SO<sub>3</sub>, which is a useful compound for pulping. Moreover, the lignin that is disadvantageous to pulping has been extracted. Therefore, this liquor could be reused to pulp.

In this treatment process, the pulping conditions of reusing treated black liquor is the key unit and the innovative point. The conditions should be optimized not only to satisfy the qualities of the prepared pulp but also to ensure that the recycled liquor has good performance of water reducing. On the basis of experiments, the optimum pulping conditions of reusing treated black liquor are shown in Table 2.

Table 2 Optimum pulping conditions of reusing treated black liquor

Materials	Alkali quantity, %	Liquor ratio	Sulfide degree, %	Cooking time, min	Maximum temperature, °C
Pine	18	1:3	15	270	170
Bamboo	16	1:3.5	10	240	165

By this pulping process, the yield of pulp came to 51.2%—51.9%, which was higher about 5%—8% than that of alkaline pulp. The hardness of pulp approximated to that of alkaline pulp 12—16.

2.5 Properties of paper made from the recycling pulp

Compared with Kraft pulp, the properties of paper made from the pulp mentioned above are also admirable, as shown in Table 3.

Table 3 Properties of paper\* made from the recycling pulp

Materials	Pulping method	Quantum, g/cm <sup>2</sup>	Rupture length, km	Avulsion index, mNm <sup>2</sup> /g	Tightness, g/cm <sup>3</sup>	Looseness, cm <sup>3</sup> /g	Whiteness, %	Opaque degree, %	Break resistance, times
Pine	Kraft*	74.0	8.55	8.46	0.56	1.79	81.5	102	402
	Recycling**	78.8	9.84	9.56	0.51	1.96	44.5	96	421
Bamboo	Kraft*	65.8	4.85	5.62	0.40	2.50	75.6	85	364
	Recycling**	60.4	5.15	5.36	0.44	2.27	47.2	92	349

Notes: \* Bleached paper provided by the papermaking factories; \*\* Not bleached

2.6 Properties of the water-reducing agent made from recycled liquor

In the process of recycling pulping, the lignin in fiber material is sulphonated into lignosulphonate, which has good performance of water reducing. Thus, the recycled liquor from the recycling pulping process can be modified to prepare water-reducing agent of concrete(Yang, 2001). Table 4 gave the test results of the properties of the water-reducing agents made from the recycled liquor under the optimum conditions. The data in Table 4 show that the property indexes of the prepared water-reducing agent have met the national standards(GB8076-1997).

Table 4 Test results of the properties of water-reducing agents

Items	Water-reducing rate, %	Difference of coagulation time, min		Ratio of pressure resistant strength, %		
		Beginning	End	3 d	7 d	28 d
Standards	≥ 5	- 90— + 120	- 90— + 120	≥ 110	≥ 110	≥ 105
Pine	7.4	+ 105	+ 110	155	147	127
Bamboo	7.0	+ 64	+ 99	143	123	120

3 Conclusions

The lignin will be almost removed completely when the black liquor is acidificaed to pH 3.5—4.0. Under the optimum flocculation conditions(temperature 70℃, time 3 h), the lignin removals of pine and bamboo black liquor reach 92.3% and 93.7% respectively.

The liquor treated by acidification and preparation can be reused to pulp. Under the optimum conditions, the yields of pulp come to 51.2%—51.9% and the properties of paper made from the pulp mentioned above are admirable.

The property indexes of the water-reducing agents prepared from recycled liquor have met the national standards.

In this treatment process, the pollution problem of black liquor in papermaking factories is solved and at the same time the useful resources are reused. Pivottally, this process is suitable for the papermaking factories with straw materials and varied scales. In short, the treatment process mentioned in this article is an effective and prospective process for solving the pollution problem of black liquor from the papermaking industry.

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